

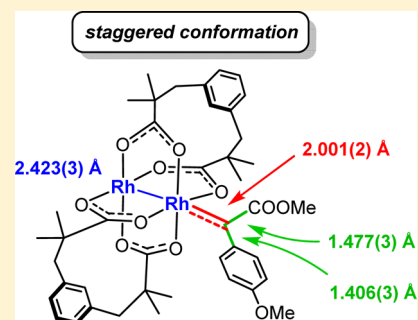
# Structures of Reactive Donor/Acceptor and Donor/Donor Rhodium Carbenes in the Solid State and Their Implications for Catalysis

Christophe Werlé, Richard Goddard, Petra Philipps, Christophe Farès, and Alois Fürstner\*

Max-Planck-Institut für Kohlenforschung, D-45470 Mülheim/Ruhr, Germany

**S** Supporting Information

**ABSTRACT:** Owing to its tremendous preparative importance, rhodium carbene chemistry has been studied extensively during past decades. The invoked intermediates have, however, so far proved too reactive for direct inspection, and reliable experimental information has been extremely limited. A series of X-ray structures of pertinent intermediates of this type, together with supporting spectroscopic data, now closes this gap and provides a detailed picture of the constitution and conformation of such species. All complexes were prepared by decomposition of a diazoalkane precursor with an appropriate rhodium source; they belong to either the dirhodium(II) tetracarboxylate carbene series that enjoys widespread preparative use, or to the class of mononuclear half-sandwich carbenes of Rh(III), which show considerable potential. The experimental data correct or refine previous computational studies but corroborate the currently favored model for the prediction of the stereochemical course of rhodium catalyzed cyclopropanations, which is likely also applicable to other reactions. Emphasis is put on stereoelectronic rather than steric arguments, with the dipole of the acceptor substituent flanking the carbene center being the major selectivity determining factor. Moreover, the very subtle influence exerted by the anionic ligands on a Rh(III) center on the chemical character of the resulting carbenes species is documented by the structures of a homologous series of halide complexes. Finally, the isolation of a N-bonded Rh(II) diazoalkane complex showcases that steric hindrance represents an inherent limitation of the chosen methodology.

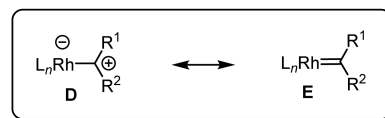
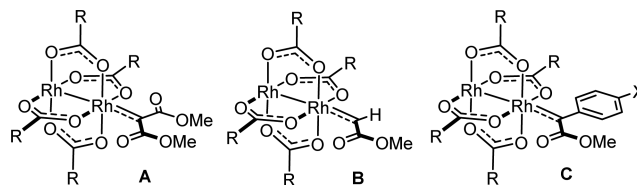


## INTRODUCTION

Since the first controlled decomposition of a diazo compound with catalytic amounts of  $\text{Rh}_2(\text{OAc})_4$ ,<sup>1,2</sup> this methodology has gained considerable importance. The resulting carbenes power a host of intra- and intermolecular bond-forming reactions or reaction cascades: For example, they engage in cyclopropanations, cyclopropanations, [4 + 3] cycloadditions, insertions into E–H (E = C, Si, O, NR, and S) and carbon-heteroatom bonds, and a myriad of ylide chemistry.<sup>3–10</sup> Many of these transformations are distinguished by impressively high turnover numbers and -frequencies as well as truly remarkable levels of chemo-, regio-, diastereo-, and enantioselectivity.<sup>3–10</sup> This is particularly true for reactions of carbenes of type C with a donor/acceptor substitution pattern that slightly tempers the “superelectrophilic” character of the pure acceptor analogues A and B.

The extensive body of preparative work on rhodium carbenes in general has led to a good qualitative understanding of their reactivity profiles. On the basis of this knowledge, it was possible to conclude, for example, that olefin cyclopropanation proceeds via a concerted but highly asynchronous mechanism.<sup>11,12</sup> This scenario puts emphasis on the resonance extreme D in which the reactive species is represented as a metal-stabilized carbocation.<sup>13</sup> Yet, even this consensus model has witnessed a striking evolution: Specifically, it had originally been assumed that an alkene approaches a donor/acceptor carbene C in a “side-on” manner while passing over the

acceptor (e.g., ester) group.<sup>14,15</sup> Today, however, the opposite trajectory is considered more plausible, invoking an “end-on”-oriented olefin traversing alongside the donor (e.g., arene) substituent (Autschbach–Davies model).<sup>12</sup> Moreover, the computed barriers along the reaction coordinate have been considerably revised over the years.<sup>16</sup>

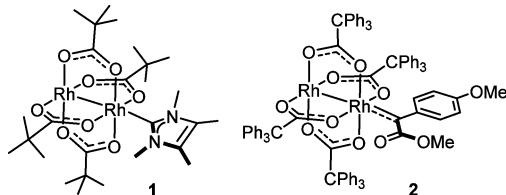


Although these amendments certainly reflect advances in computational chemistry,<sup>11,12,17</sup> they also emphasize the lack of experimental calibration points. Relevant dirhodium carbenes largely defied direct inspection. Only the X-ray structures of various NHC adducts such as **1** are known.<sup>18,19</sup> Although **1** misses the prototypical reactivity of electrophilic carbenes, the

Received: December 21, 2015

Published: February 24, 2016

lengthening of the Rh–Rh bond concurs with a three-center/four-electron bonding mode that is currently thought to be the best description of the dimetallic core.<sup>20,21</sup> Only very recently have Davies, Berry, and co-workers managed to observe prototype push/pull dirhodium carbene **2** in solution.<sup>22</sup> The characteristic signal at  $\delta_C = 242$  ppm showcases the electrophilic nature of this species, whereas the recorded EXAFS data suggest a linear Rh–Rh–C array and an elongated Rh–Rh bond (2.43 Å). The averaged Rh–C and Rh–O distances derived from the EXAFS spectra were deconvoluted by DFT to individual bond lengths of 1.972 and 2.041 Å, respectively.<sup>22</sup> Relevant conformational details, however, could not be deduced.



Outlined below is a series of crystal structures of reactive carbenes of the Rh(II) tetracarboxylate as well as of the Rh(III) half-sandwich type with different substitution patterns. This includes the donor/acceptor complex **10**, which differs from **2** only in that it carries a  $\alpha,\alpha,\alpha',\alpha'$ -tetramethyl-1,3-benzenedipropionate (esp)<sup>23</sup> rather than triphenylacetate (tpa)<sup>24</sup> ligand set; esp ligands have an impressive track record in rhodium catalysis.<sup>23,25</sup> Collectively, our data provide a detailed picture of the constitution, conformation, and bonding of these important reactive intermediates; they allow the published computational data to be validated and the predictive models to be checked.<sup>26</sup>

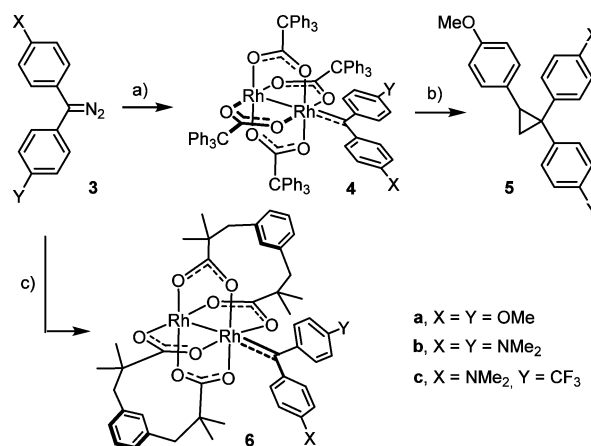
## RESULTS AND DISCUSSION

**Donor/Donor Series.** Because donor substituents are known to tame an adjacent electrophilic carbene center, it seemed reasonable to start our structural investigations by targeting dirhodium carbenes bearing two donor groups.<sup>27</sup> The bis(*p*-methoxyphenyl)carbene backbone was deemed a good candidate, not least because this particular motif had allowed us to isolate the first reactive gold carbenes in crystalline form.<sup>28,29</sup> Our efforts were invigorated by a control experiment, which showed that the reaction of readily prepared and safe-to-handle bis(4-methoxyphenyl)-diazomethane **3a**<sup>30,31</sup> with 4-methoxystyrene in the presence of  $[\text{Rh}_2(\text{tpa})_4] \cdot \text{CH}_2\text{Cl}_2$  (0.5 mol %) cleanly furnished the desired cyclopropane derivative **5a** (Scheme 1). This result proves that the putative carbene **4a** generated in situ shows the prototype chemical behavior of this class of reactive intermediates;<sup>32,33</sup> its structure is therefore undoubtedly relevant for mechanistic discussions.

Treatment of a cold green solution of  $[\text{Rh}_2(\text{tpa})_4] \cdot \text{CH}_2\text{Cl}_2$  in  $\text{CH}_2\text{Cl}_2$  with a purple solution of **3a** in the same solvent resulted in an instantaneous color change to dark turquoise and the vigorous evolution of  $\text{N}_2$ . The resulting species **4a** turned out to be sufficiently stable at  $-20$  °C for characterization by NMR, UV, IR, and even HRMS (ESI+). The resonance at  $\delta_C = 268.9$  ppm bears witness for its carbene character; somewhat counterintuitively though, this signal is downfield from that of push/pull complex **2** ( $\delta_C = 242$  ppm) observed by Davies, Berry, and co-workers.<sup>22</sup>

After numerous attempts, we managed to grow crystals of **4a** suitable for X-ray diffraction. Major difficulties arose from the fact that even the pure crystalline material decomposes in less

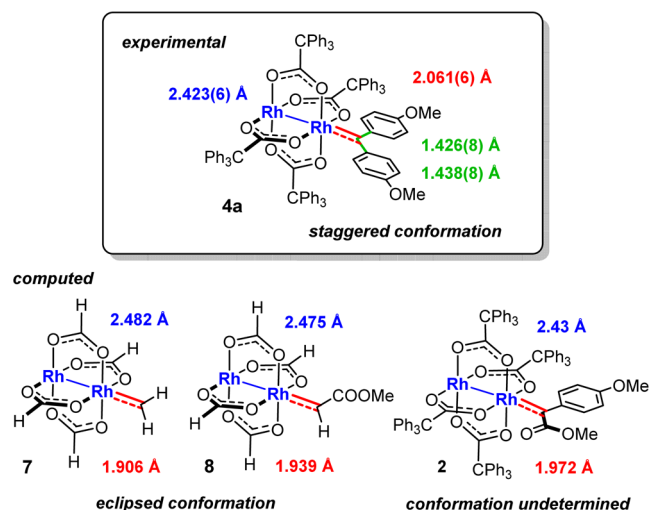
## Scheme 1. Preparation of Dirhodium Tetracarboxylate Complexes and Their Use in Olefin Cyclopropanation<sup>a</sup>



<sup>a</sup>Reagents and conditions: (a)  $[\text{Rh}_2(\text{tpa})_4] \cdot \text{CH}_2\text{Cl}_2$ ,  $\text{CH}_2\text{Cl}_2$ ,  $-10$  °C; (b) *p*-methoxystyrene, pentane, see text; and (c)  $[\text{Rh}_2(\text{esp})_2]$ ,  $\text{CH}_2\text{Cl}_2$ ,  $-10$  °C.

than 12 h at  $-20$  °C; solute  $\text{CH}_2\text{Cl}_2$  and toluene are necessary to ensure metastability yet tend to be highly disordered within the unit cell. Considerable experimentation was necessary to find that crystals grown from the ternary mixture  $\text{CH}_2\text{Cl}_2$ /toluene/fluorobenzene were of better quality, allowing all atoms of the complex to be refined anisotropically ( $R = 5.9\%$ ).

Because the structure of **4a** in the solid state has been published in a recent communication,<sup>26</sup> it suffices to briefly summarize the relevant attributes (Figure 1). As expected, the



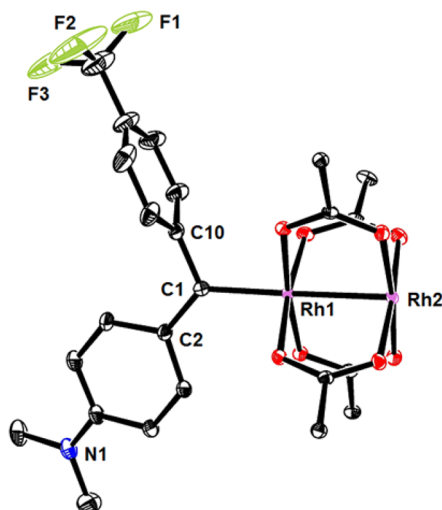
**Figure 1.** Comparison of important structural features of complex **4a** with in silico data.

carbene ligand occupies an axial coordination site on the dirhodium cage and the Rh2–Rh1–C1 axis is almost linear ( $176.9^\circ$ ). The Rh1–C1 bond distance (2.061(6) Å) is substantially longer than that computed for model compounds **7** (1.906 Å)<sup>20</sup> and **8** (1.939 Å)<sup>20</sup> and even hemistabilized carbene **2** (1.972 Å).<sup>22</sup> This fact suggests that back-donation of electron density from the metal into the carbene center is low. To compensate, C1 strongly engages with the flanking arenes, one of which is coplanar to ensure maximum orbital overlap. This tight interaction leads to a significant contraction of the

bonds between C1 and the C<sub>ipso</sub> atoms (1.426(8)/1.438(8) Å). The entire carbene substituent adopts a staggered conformation relative to the O–Rh–O unit, an aspect to be discussed in more detail below, whereas **7** and **8** were computed to prefer the eclipsing orientation.<sup>20</sup>

The analogous complexes **4b** and **6b** have also been obtained in crystalline form, which carry –NMe<sub>2</sub> rather than –OMe groups on the arene rings and differ from each other in the ancillary tetracarboxylate ligand set (tpa in **4** versus esp in **6**). Their basic structural attributes are largely similar to those of **4a**, with a staggered conformation of the carbene entities relative to the dimetallic core and a strong participation of the electron rich arenes in the stabilization of the carbene center. (X-ray structures of **4b** and **6b** are displayed in the Supporting Information.) A subtle and as yet unexplained difference, however, relates to the fact that **4a** and **6b** crystallize as coordination polymers, in which the –OMe (–NMe<sub>2</sub>) group of one monomer unit ligates Rh2 of the next unit, whereas **4b** is monomeric in the unit cell.

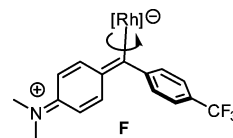
**Donor/Acceptor Series.** Next, we prepared complex **4c** in which one electron-rich and one electron-deficient phenyl ring flank the carbene center. The structure of this particular push/pull dirhodium carbene in the solid state is informative (Figure 2). As one might expect, the phenyl ring with the –NMe<sub>2</sub>



**Figure 2.** Structure of donor/acceptor dirhodium carbene **4c** in the solid state; the lateral phenyl rings of the tpa ligands on the dimetallic cage are removed for clarity. (For the complete structure and further details, see the Supporting Information.)

substituent carries the burden of stabilizing the carbene center; it adopts an almost perfectly coplanar orientation ( $\Theta = 0.9^\circ$ ) to maximize overlap of the  $\pi$  cloud of the phenyl ring with the (empty) carbene p orbital, representing the major lobe of the LUMO. With only 1.389(3) Å, the C1–C2 distance is even shorter than the already very tight C1–C<sub>ipso</sub> bonds in **4a** (Figure 1). The F<sub>3</sub>CC<sub>6</sub>H<sub>4</sub>– ring as the acceptor substituent, in contrast, lies orthogonal to the carbene center ( $\Theta = -94.7^\circ$ ) to largely cutoff any destabilizing electronic communication. As a consequence, the C1–C10 bond (1.476(3) Å) is significantly longer than C1–C2. Once again, the carbene entity adopts a staggered orientation relative to the dinuclear core. The structural features of the analogous complex **6c** endowed with esp rather than tpa ligands are largely similar. (For details, see the Supporting Information.) This comparison confirms

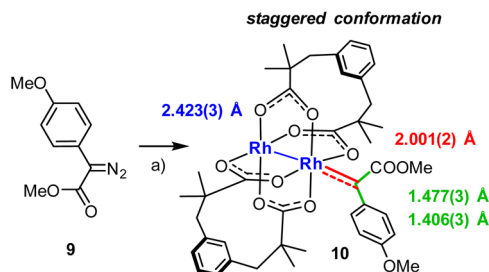
that the choice of ancillary ligands exerts only a small effect on the structure of such dirhodium species.



The NMR data suggest that the structure of these complexes in solution must be very similar. Most notably, the rotation about the C1–C2 bond in **4c** and **6c** is largely frozen out at  $-10^\circ\text{C}$ , and the species are best depicted by the quinoid resonance extreme F. In addition to the inequivalent protons of the Me<sub>2</sub>NC<sub>6</sub>H<sub>4</sub>– ring, the characteristic <sup>15</sup>N NMR shift of the Me<sub>2</sub>N– group ( $\delta_{\text{N}} = -282.6$  ppm) is in excellent agreement with this description.<sup>34</sup> However, the rotation about the Rh1–C1 bond is unrestricted on the NMR time scale, which confirms the low bond order of the carbene unit deduced from the crystallographic data.

Particularly noteworthy is the structure of complex **10** in the solid state, which represents a prototype donor/acceptor carbene of the type that has been most widely studied in the past (Scheme 2).<sup>67,35</sup> **10** is the esp-analogue of the tpa complex

#### Scheme 2. Preparation of Prototypical Donor/Acceptor Dirhodium Tetracarboxylate Complex **10** and Summary of Relevant Structural Data<sup>a</sup>

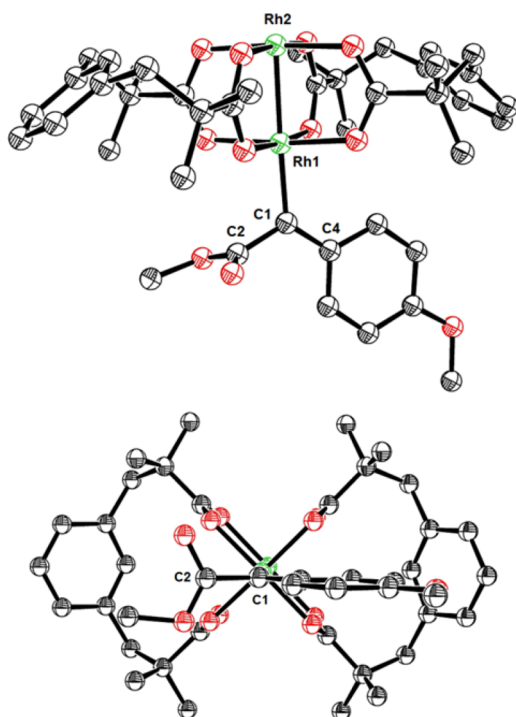


<sup>a</sup>Reagents and conditions: [Rh<sub>2</sub>(esp)<sub>2</sub>], FC<sub>6</sub>H<sub>5</sub>/CH<sub>2</sub>Cl<sub>2</sub>, 0 °C →  $-20^\circ\text{C}$

**2**, which could previously only be characterized by spectroscopic means.<sup>22</sup> Because the data outlined above suggest that the change of the ancillary ligand set has little structural bearing, the high-quality X-ray data ( $R = 3.18\%$ ) of this very labile intermediate are considered an important reference point (Figure 3). This notion is supported by the fact that the carbene centers of **10** ( $\delta_{\text{C}} = 237.1$  ppm) and of **2** ( $\delta_{\text{C}} = 242$  ppm)<sup>22</sup> resonate at very similar fields.

The donor substituent is perfectly coplanar with the carbene center ( $\Theta = 0^\circ$ ); accordingly, the C1–C4 bond is very short (1.406(3) Å). The fact that all protons on the arene ring are inequivalent in the <sup>1</sup>H NMR spectrum recorded at  $-50^\circ\text{C}$  suggests that this structure-determining motif is retained in solution whereas the rotation about the Rh1–C1 carbene bond is unrestricted at this temperature. In contrast, the ester is orthogonally oriented, such that the C1–C2 distance is contracted (1.477(3) Å).

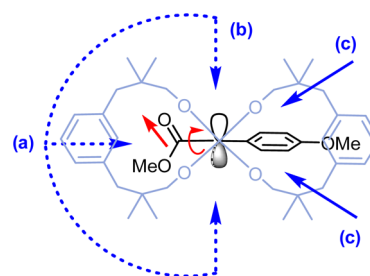
With regard to the carbene ligand itself, it is noteworthy that the Rh1–C1 bond in **10** (2.001(2) Å) clearly exceeds the 1.972 Å computed for **2** whereas the Rh2–Rh1 distance (2.4226(3) Å) is somewhat shorter than the 2.43 Å proposed for **2** on the basis of EXAFS/DFT.<sup>22</sup> The mutual compensation of the bond lengths within the core is readily understood on the basis of a



**Figure 3.** Structure of donor/acceptor dirhodium carbene **10** in the solid state in two different orientations; for details, see the Supporting Information.

three-center/four-electron bonding mode for the Rh–Rh–C unit.<sup>20,21</sup> Another interesting and as yet undescribed aspect concerns the asymmetry of the bond angles about the carbene center: Although the arene ring is visibly bent away from the cage (Rh1–C1–C4, 127.6(1)°), likely to avoid a clash with the tetracarboxylate ligand framework, the orthogonally disposed ester group is hardly sterically inflicting as evident from the small Rh1–C1–C2 angle (113.7(2)°).

The two esp ligands orient their meta-disubstituted benzene rings in a syn fashion, such that the dimetallic core adopts  $C_s$  symmetry; it is noteworthy that this conformation is different from that of  $[\text{Rh}_2(\text{esp})_2](\text{acetone})_2$  which is  $C_2$  symmetric.<sup>23</sup> Once again, the carbene entity is staggered relative to the O–Rh–O unit, formally bisecting the binding pocket created by the ancillary ligands (Figure 3, bottom). Provided this orientation is retained in solution, it is safe to predict that an olefin (or other nucleophilic reaction partner) will hardly be able to approach the (empty) carbene lobe by passing over the ester (Figure 4). Though sterically unhindered, trajectory (a) is stereoelectronically unfavorable and does not lead to efficient orbital overlap. The seemingly most open trajectory (b) is equally unlikely on stereoelectronic grounds because of massive dipole–dipole repulsion between the ester carbonyl and the incoming nucleophile. Therefore, it is probable that the reaction partner approaches the carbene center in a Bürgi–Dunitz-type trajectory by gliding alongside the arene, which itself is no obstacle in the orientation that it adopts. The structure of **10** in the solid state therefore lends credence to the Autschbach–Davies model currently favored in predicting the stereochemical course of reactions involving dirhodium tetracarboxylate carbenes derived from aryldiazoacetates, which generally provide excellent diastereoselectivities in reactions with olefins or other partners.<sup>12,36</sup>



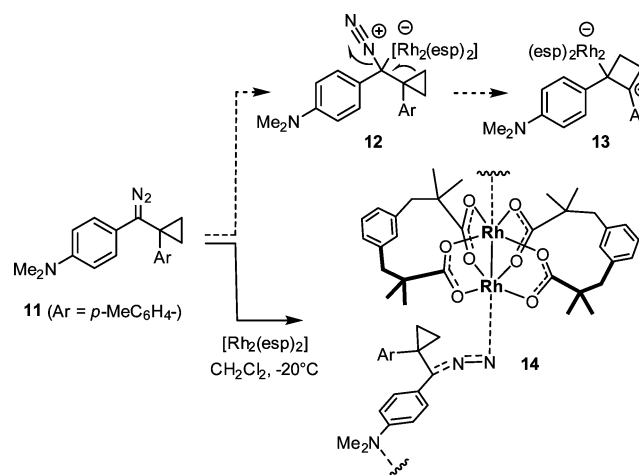
**Figure 4.** Newman-type projection of complex **10** along the C1–Rh1–Rh2 bond. The blue arrows show possible trajectories for an incoming nucleophile; the straight red arrow indicates the dipole of the acceptor group. For the unhindered rotation of the ester (curved red arrow), any backside attack will face the same stereoelectronic demands.

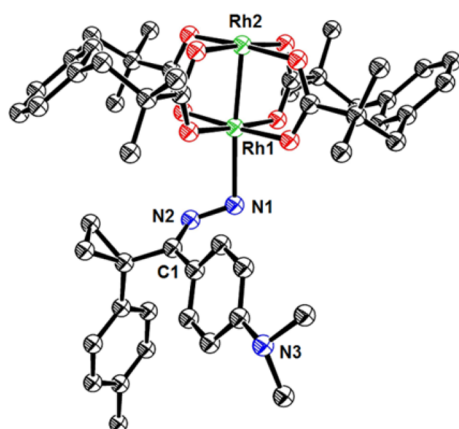
As outlined above, the structure of the donor/acceptor carbenes **4c** and **6c** bearing two aryl groups of different electronic character are largely similar to that of **10**. Even though the dipole of the  $\text{F}_3\text{CC}_6\text{H}_4-$  ring acting as the acceptor substituent in lieu of the ester is orthogonal rather than parallel to the carbene p orbital, trajectories (a) and (b) remain stereoelectronically disfavored. Therefore, one can expect the reaction of *p*-methoxystyrene with diaryl diazomethane **3c** catalyzed by  $[\text{Rh}_2(\text{esp})_2]$  to provide cyclopropane **5c** with excellent selectivity (Scheme 1); this is indeed the case (dr >98:2, NMR).<sup>37</sup>

**Limitations.** The diazomethane derivative **11** was conceived as an appropriate substrate in an attempt to probe the chemical character of the resulting rhodium carbene. Any strong contribution of a bipolar resonance extreme **D** would impart non-classical carbocation character onto the derived carbene.<sup>38,39</sup> If so, then ring opening of the cyclopropyl unit or, more likely, ring expansion is expected to occur because cyclobutyl cation resonance form **13** seems most favored for the extra benzylic stabilization (Scheme 3).

However, the attempted formation of a carbene complex failed; rather, adduct **14** was isolated (as a coordination polymer in the solid state), in which the intact diazo group is ligated end-on to the dirhodium fragment (Figure 5).<sup>40</sup> The doubly bent coordination geometry positions the substituents on the N atoms quasi-orthogonal to each other (Rh1–N1–

**Scheme 3.** Attempted Formation of a Rhodium Carbene, which Led to the Isolation of a Diazo Adduct





**Figure 5.** Structure of the diazo adduct **14** in the solid state; for details, see the Supporting Information.

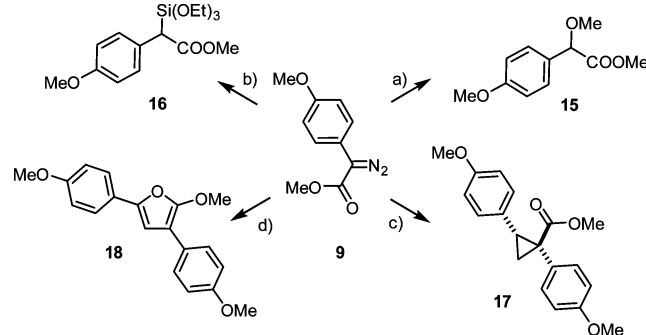
$\text{N2}-\text{C1} = 108.2^\circ$ ).<sup>41</sup> The failure to form a rhodium carbene is ascribed to steric hindrance, which prevents bulky  $[\text{Rh}_2(\text{esp})_2]$  from reaching the negatively polarized C atom of **11** with formation of **12** as the necessary first step en route to a metalcarbene.<sup>42</sup> Under more forcing conditions, substrate **11** decomposed; therefore the envisaged chemical interrogation of rhodium carbenes with the help of suitable reporter groups must await future studies.

#### Rhodium(III) Half-Sandwich Carbene Complexes.

Although the use of the dinuclear Rh(II) tetracarboxylate carbenes A–C dominates the field, not least because they are easily rendered chiral, it is well-established that various Rh(I) as well as Rh(III) sources also lead to carbenes with useful reactivity profiles.<sup>1,2,43,44</sup> A potentially interesting class is that of the Rh(III) carbenes of the half-sandwich type, which are invoked in a large body of (directed) C–H activation chemistry for the (late-stage) functionalization of various heterocyclic scaffolds.<sup>45–47</sup> They are usually prepared from  $[\text{Cp}^*\text{RhX}_2]_2$  and an appropriate diazo precursor (frequently in combination with a soluble Ag(I) salt to abstract the chloride ligands from the active species). It is believed, however, that the highly electrophilic metal fragment (cyclo)metalates the chosen arene substrate before it actually reacts with the diazo derivative.<sup>45–47</sup>

This very large and rapidly growing body of work stands in contrast to the lack of information about proper piano-stool Rh(III) carbenes devoid of a cyclometalated backbone; yet such species exhibit excellent reactivity (Scheme 4). An unoptimized loading of 1 mol % sufficed for typical O–H or Si–H insertions to proceed in excellent yield. The cyclopropanation of 4-methoxystyrene also worked well, provided that  $[\text{Cp}^*\text{RhI}_2]_2$  was chosen as the precatalyst, whereas  $[\text{Cp}^*\text{RhCl}_2]_2$  proved markedly less efficient. (See below for a possible explanation of this different behavior.) Particularly noteworthy is the direct formation of alkoxyfuran **18** on reaction of **9** with (4-methoxyphenyl)acetylene; in judging the outcome, one has to keep in mind that this particular product is prone to hydrolysis on work up. In any case, terminal alkynes usually afford cyclopropenes in the first place, which can be rearranged to (alkoxy)furan derivatives in a separate step.<sup>4–9,48</sup> Although this reactivity pattern has ample precedent in the acceptor/acceptor series, the few recorded examples for donor/acceptor carbenes tend to be low-yielding.<sup>49</sup> Therefore, the direct formation of **18** is an interesting lead, not least because such electron-rich furan derivatives have promising follow-up chemistry.<sup>50</sup>

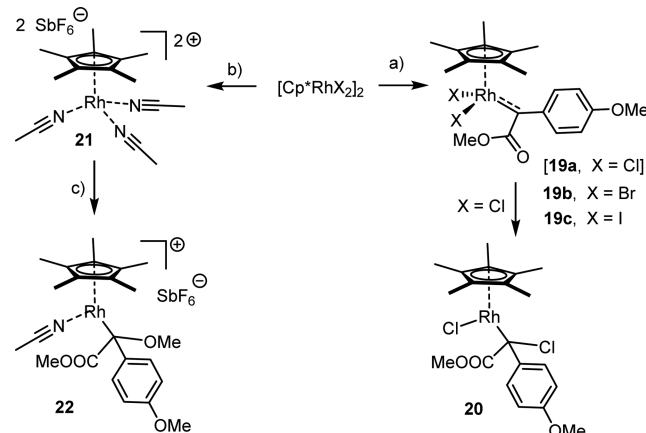
#### Scheme 4. Reactivity of a Piano-Stool Rh(III) Carbene Generated in Situ<sup>a</sup>



<sup>a</sup>Reagents and conditions: (a)  $[\text{Cp}^*\text{RhI}_2]_2$  (1 mol %),  $\text{CH}_2\text{Cl}_2$ , MeOH, 88%; (b)  $[\text{Cp}^*\text{RhI}_2]_2$  (1 mol %),  $(\text{EtO})_3\text{SiH}$ ,  $\text{CH}_2\text{Cl}_2$ , 81%; (c) *p*-methoxystyrene, pentane, 69% (with  $[\text{Cp}^*\text{RhI}_2]_2$  (1 mol %)); 46% (with  $[\text{Cp}^*\text{RhCl}_2]_2$  (1 mol %)); (d)  $[\text{Cp}^*\text{RhI}_2]_2$  (1 mol %), (*p*-methoxyphenyl)acetylene,  $\text{CH}_2\text{Cl}_2$ , 65%

Secure structural information about any type of half-sandwich Rh(III) carbene is missing. The higher oxidation state of the central rhodium atom and the lack of an adjuvant second metal center, as present in A–C, suggest that the resulting mononuclear carbenes might be even less stable. In line with this notion, no carbene signal was detected by <sup>13</sup>C NMR in the reaction of  $[\text{Cp}^*\text{RhCl}_2]_2$  with aryldiazoester **9** (Scheme 5), but a new resonance appeared at 70.6 ppm. It was

#### Scheme 5. Preparation of Rh(III) Half-Sandwich Carbene Complexes<sup>a</sup>



<sup>a</sup>Reagents and conditions: (a) **9**,  $\text{FC}_6\text{H}_5/\text{CH}_2\text{Cl}_2$ ,  $0^\circ\text{C} \rightarrow -20^\circ\text{C}$ ; (b) 2  $\text{AgSbF}_6$ , MeCN; and (c) **9**, MeOH,  $0^\circ\text{C} \rightarrow -20^\circ\text{C}$

not clear at the outset whether this observation reflected inherent chemical issues or was simply caused by the instability of the complex, which decomposes in solution in <1.5 h at  $-50^\circ\text{C}$ . An X-ray structure clarified the point: As can be seen from Figure 6, push/pull carbene **19a** generated in situ has inserted into one of the Rh–Cl bonds, resulting in the formation of chloroalkyl species **20**. This species can be viewed as a functionalized C-metalated rhodium enolate, chiral at metal and at the metalated C atom; it is formed as a single diastereomer.<sup>51,52</sup> To compensate for the loss of an anionic ligand, the now formally 16-electron Rh(III) center engages with the aromatic ring, as evident from the short contacts to the ipso C atoms and one of the ortho C atoms. This interaction

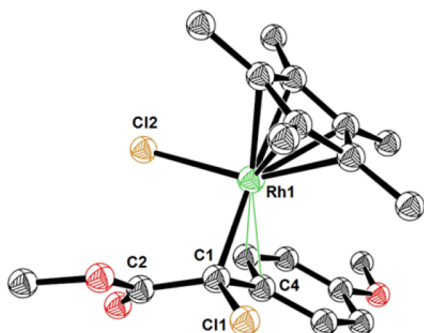


Figure 6. Structure of chloroalkyl complex **20** in the solid state.

likely persists in solution as suggested by the high-field shift of the corresponding C atoms (broad signals at  $\sim 94$  and  $\sim 116$  ppm). The comparatively long Rh1–C1 (2.1226(12) Å) and C1–C4 (1.4666(17) Å) bonds clearly reflect the loss of true carbene character. (Note that **20** is still “carbenoid” in the sense that it contains a carbon atom carrying at the same time a metal and a leaving group.)

The formation of **20** is thought to illustrate the exceptional electron demand of the transient Rh(III) carbene **19a**, which engenders the halide shift at low temperature. This internal quenching mechanism might well explain why most catalytic transformations based on the decomposition of a diazoester derivative with  $[\text{Cp}^*\text{RhCl}_2]_2$  use silver salts as additives, which likely prevent such halide shifts from occurring and allows nucleophilic partners to react with the carbene center.<sup>45–47</sup> This hypothesis is corroborated by the outcome of the reaction of aryldiazoacetate **9** with cationic rhodium precursor **21** (Scheme 5). In line with our expectations, the clean formation of the corresponding cationic methyl ether derivative **22** was observed, which proves that the transient rhodium carbene devoid of the potentially interfering chloride ligands is trapped by the external nucleophile MeOH chosen as the reaction medium. Complex **22** also represents a functionalized, C-metalated and chiral Rh(III) enolate; its structure is similar to that of chloroalkyl species **20** even with regard to the interaction of the metal center with the electron rich arene (Figure 7).

In this context, it is also noteworthy that a complex related to the chloroalkyl species **20** has previously been inferred from spectroscopic data. Thus, reaction of *iodo*-rhodium(III) tetra-

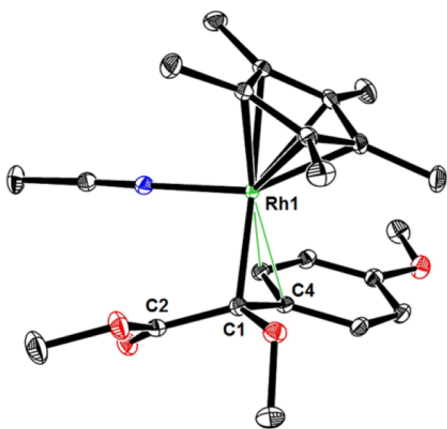


Figure 7. Structure of methanol adduct **22** in the solid state; only the complex cation is shown for clarity.

tolylporphyrin with ethyl diazoacetate was proposed to afford an *iodo*alkyl complex that failed to cyclopropanate styrene.<sup>53,54</sup>

In view of this precedent, it seemed reasonable to assume that the reaction of **9** with  $[\text{Cp}^*\text{RhX}_2]_2$  (X = Br and I) in lieu of  $[\text{Cp}^*\text{RhCl}_2]_2$  should also result in halide migration with formation of the corresponding haloalkyl species. Surprisingly, however, corresponding carbene complexes **19b,c** were the major species (Scheme 5). Of note is their highly deshielded carbene center ( $\delta_{\text{C}} = 314.2$  ppm, X = Br; 316.4 ppm, X = I), which resonates downfield from that in the dirhodium(II) donor/acceptor carbene **10** ( $\delta_{\text{C}} = 237.1$  ppm).

The constitution of **19b,c** was unambiguously established by X-ray diffraction (Figure 8; for the dibromo complex **19b**, see

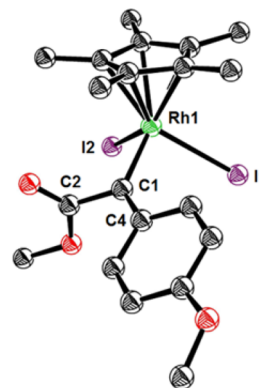


Figure 8. Structure of half-sandwich donor/acceptor Rh(III) carbene **19c** in the solid state.

the Supporting Information). As expected, the arene as the donor substituent is coplanar with the carbene center ( $\Theta = 0.5^\circ$ ) to maximize orbital overlap, whereas the plane of the ester is essentially perpendicular to it ( $\Theta = 100.0^\circ$ ). Along with this comes a contracted C1–C4 bond (1.415(4) Å) but a long C1–C2 (1.504(4) Å) bond; at only 1.970(3) Å, the Rh1–C1 bond is visibly shorter than the analogous carbene distances in the dirhodium(II) tetracarboxylate complexes outlined above. The fact that the nature of the anionic ligand determines whether a true carbene (**19b,c**) or a “carbenoid” (**20**) is passed through illustrates an as yet hardly recognized way to control rhodium-catalyzed reactions of diazo compounds. The better performance of  $[\text{Cp}^*\text{RhI}_2]_2$  as compared to that of  $[\text{Cp}^*\text{RhCl}_2]_2$  in the cyclopropanation shown in Scheme 4 likely reflects this aspect.

## CONCLUSIONS

The tremendous importance of rhodium carbene chemistry in general stands in striking contrast to the lack of experimental data concerning the structure of the relevant intermediates. For their pronounced electrophilicity, such species are highly unstable and therefore largely defy direct inspection by spectroscopic or crystallographic means. This difficulty notwithstanding, we are able to present a series of crystal structures of dinuclear tetracarboxylate complexes of Rh(II) as well as mononuclear half-sandwich complexes of Rh(III), which are by far the most commonly used intermediates in this field. We provide an unprecedentedly close look at representative members of these families and reveal many conformational details that could hitherto only be inferred from indirect evidence and/or in silico data. The experimental results refine the understanding of their gross structural attributes and correct pertinent bond lengths, which had previously been

deduced from computational studies at different levels of theory. A recurrent theme in these X-ray structures is the staggered orientation of the carbene unit relative to the dirhodium tetracarboxylate core carrying the ancillary ligands. This trait is critically important for the understanding of the diastereo- and enantioselective course of rhodium-catalyzed reactions of diazoalkanes. Although our data suggest that stereoelectronic (rather than purely steric) factors play a decisive role, the basic concept of the currently favored predictive model is validated.<sup>12</sup> Finally, it is shown how the anionic ligands present in half-sandwich Rh(III) carbenes regulate the electrophilicity of reactive intermediates of this type. Thus, the seemingly subtle change from bromide (or iodide) to chloride dramatically alters the chemical nature of the resulting complexes from a prototype carbene to a chloroalkyl species. This insight allows the common use of silver additives in reactions of diazoesters catalyzed by  $[\text{Cp}^*\text{RhCl}_2]_2$  to be rationalized.

## ■ ASSOCIATED CONTENT

### ● Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/jacs.5b13321.

Experimental details including characterization data, copies of NMR spectra of new compounds, and crystallographic information concerning the structures of complexes **4b**, **4c**, **6b**, **6c**, **10**, **14**, **19b**, **19c**, **20** and **22** in the solid state. (PDF)

Crystallographic information file for complexes **4b**, **4c**, **6b**, **6c**, **10**, **14**, **19b**, **19c**, **20** and **22** in the solid state. (CIF)

## ■ AUTHOR INFORMATION

### Corresponding Author

\*fuerstner@kofo.mpg.de

### Notes

The authors declare no competing financial interest.

## ■ ACKNOWLEDGMENTS

Generous financial support by the MPG is gratefully acknowledged. We thank all analytical departments of our Institute for excellent support as well as Umicore AG & Co KG, Hanau, for a generous gift of noble metal salts.

## ■ REFERENCES

- (1) Paulissen, R.; Reimlinger, H.; Hayez, E.; Hubert, A. J.; Teyssié, P. *Tetrahedron Lett.* **1973**, *14*, 2233–2236.
- (2) (a) Hubert, A. J.; Noels, A. F.; Anciaux, A. J.; Teyssié, P. *Synthesis* **1976**, 1976, 600–602. (b) Démonceau, A.; Noels, A. F.; Hubert, A. J.; Teyssié, P. *J. Chem. Soc., Chem. Commun.* **1981**, 688–689.
- (3) Doyle, M. P.; McKervey, M. A.; Ye, T. *Modern Catalytic Methods for Organic Synthesis with Diazo Compounds: From Cyclopropanes to Ylides*; Wiley: New York, 1998.
- (4) Evans, P. A., Ed. *Modern Rhodium Catalyzed Organic Reactions*; Wiley-VCH: Weinheim, 2005.
- (5) (a) Padwa, A.; Weingarten, M. D. *Chem. Rev.* **1996**, *96*, 223–269. (b) Padwa, A. *Chem. Soc. Rev.* **2009**, *38*, 3072–3081.
- (6) Davies, H. M. L.; Antoulinakis, E. G. *Org. React.* **2001**, *57*, 1–326.
- (7) (a) Davies, H. M. L.; Beckwith, R. E. *J. Chem. Rev.* **2003**, *103*, 2861–2904. (b) Davies, H. M. L.; Manning, J. R. *Nature* **2008**, *451*, 417–424. (c) Davies, H. M. L.; Morton, D. *Chem. Soc. Rev.* **2011**, *40*, 1857–1869. (d) Davies, H. M. L.; Lian, Y. *Acc. Chem. Res.* **2012**, *45*, 923–935.

- (8) (a) Doyle, M. P. *Chem. Rev.* **1986**, *86*, 919–939. (b) Doyle, M. P.; Forbes, D. C. *Chem. Rev.* **1998**, *98*, 911–935. (c) Doyle, M. P.; Duffy, R.; Ratnikov, M.; Zhou, L. *Chem. Rev.* **2010**, *110*, 704–724.

- (9) (a) Lebel, H.; Marcoux, J.-F.; Molinaro, C.; Charette, A. B. *Chem. Rev.* **2003**, *103*, 977–1050. (b) Zhang, Y.; Wang, J. *Coord. Chem. Rev.* **2010**, *254*, 941–953. (c) Ye, T.; McKervey, M. A. *Chem. Rev.* **1994**, *94*, 1091–1160. (d) Gois, P. M. P.; Afonso, C. A. M. *Eur. J. Org. Chem.* **2004**, *2004*, 3773–3788. (e) Zhang, Z.; Wang, J. *Tetrahedron* **2008**, *64*, 6577–6605. (f) Ford, A.; Miel, H.; Ring, A.; Slattery, C. N.; Maguire, A. R.; McKervey, M. A. *Chem. Rev.* **2015**, *115*, 9981–10080. (g) DeAngelis, A.; Panish, R.; Fox, J. M. *Acc. Chem. Res.* **2016**, *49*, 115–127. (h) Gillingham, D.; Fei, N. *Chem. Soc. Rev.* **2013**, *42*, 4918–4931. (i) Zhu, S.-F.; Zhou, Q.-L. *Acc. Chem. Res.* **2012**, *45*, 1365–1377. (j) Guo, X.; Hu, W. *Acc. Chem. Res.* **2013**, *46*, 2427–2440. (k) Murphy, G. K.; Stewart, C.; West, F. G. *Tetrahedron* **2013**, *69*, 2667–2686.

- (10) For the preparation of metal carbenes by the decomposition of precursors other than diazoalkanes, see (a) Gulevich, A. V.; Gevorgyan, V. *Angew. Chem., Int. Ed.* **2013**, *52*, 1371–1373. (b) Davies, H. M. L.; Alford, J. S. *Chem. Soc. Rev.* **2014**, *43*, 5151–5162. (c) Anbarasan, P.; Yadagiri, D.; Rajasekar, S. *Synthesis* **2014**, *46*, 3004–3023. (d) Wang, Y.; Lei, X.; Tang, Y. *Synlett* **2015**, *26*, 2051–2059. (e) Barluenga, J.; Valdés, C. *Angew. Chem., Int. Ed.* **2011**, *50*, 7486–7500. (f) Shao, Z.; Zhang, H. *Chem. Soc. Rev.* **2012**, *41*, 560–572.

- (11) This proposal is in accord with the observed kinetic isotope effects and supported by computational studies; see Nowlan, D. T.; Gregg, T. M.; Davies, H. M. L.; Singleton, D. A. *J. Am. Chem. Soc.* **2003**, *125*, 15902–15911.

- (12) Hansen, J.; Autschbach, J.; Davies, H. M. L. *J. Org. Chem.* **2009**, *74*, 6555–6563.

- (13) The conceivable alternative pathway invoking the true carbene resonance form **E** that undergoes a [2 + 2] cycloaddition with formation of a metallacyclobutane followed by reductive elimination is unlikely in the case of rhodium; for a general discussion of this mechanistic scenario, see Brookhart, M.; Studabaker, W. B. *Chem. Rev.* **1987**, *87*, 411–432.

- (14) Davies, H. M. L.; Bruzinski, P. R.; Lake, D. H.; Kong, N.; Fall, M. J. *J. Am. Chem. Soc.* **1996**, *118*, 6897–6907.

- (15) See also (a) Doyle, M. P.; Griffin, J. H.; Bagheri, V.; Dorow, R. L. *Organometallics* **1984**, *3*, 53–61. (b) O'Bannon, P. E.; Dailey, W. P. *J. Org. Chem.* **1989**, *54*, 3096–3101. (c) Brown, K. C.; Kodadek, T. J. *Am. Chem. Soc.* **1992**, *114*, 8336–8338.

- (16) The barrier for the cyclopropanation of styrene with a vinylcarbene was originally computed as 0.5 kcal/mol (ref 11), which was later deemed inconsistent with experimental data; a subsequent study found a barrier of no less than 4.5 kcal/mol for the analogous reaction of a closely related phenylcarbene (cf. ref 12).

- (17) For further pertinent in silico studies into various types of rhodium carbenes at different levels of theory, see (a) Doyle, M. P.; Winchester, W. R.; Hoorn, J. A. A.; Lynch, V.; Simonsen, S. H.; Ghosh, R. J. *Am. Chem. Soc.* **1993**, *115*, 9968–9978. (b) Pirrung, M. C.; Morehead, A. T., Jr. *J. Am. Chem. Soc.* **1994**, *116*, 8991–9000. (c) Sheehan, S. M.; Padwa, A.; Snyder, J. P. *Tetrahedron Lett.* **1998**, *39*, 949–952. (d) Padwa, A.; Snyder, J. P.; Curtis, E. A.; Sheehan, S. M.; Worsencroft, K. J.; Kappe, C. O. *J. Am. Chem. Soc.* **2000**, *122*, 8155–8167. (e) Yoshikai, N.; Nakamura, E. *Adv. Synth. Catal.* **2003**, *345*, 1159–1171. (f) Nowlan, D. T.; Singleton, D. A. *J. Am. Chem. Soc.* **2005**, *127*, 6190–6191. (g) Liang, Y.; Zhou, H.; Yu, Z.-X. *J. Am. Chem. Soc.* **2009**, *131*, 17783–17785. (h) Hansen, J. H.; Gregg, T. M.; Ovalles, S. R.; Lian, Y.; Autschbach, J.; Davies, H. M. L. *J. Am. Chem. Soc.* **2011**, *133*, 5076–5085. (i) Hansen, J. H.; Parr, B. T.; Pelphrey, P.; Jin, Q.; Autschbach, J.; Davies, H. M. L. *Angew. Chem., Int. Ed.* **2011**, *50*, 2544–2548.

- (18) (a) Snyder, J. P.; Padwa, A.; Stengel, T.; Arduengo, A. J.; Jockisch, A.; Kim, H.-J. *J. Am. Chem. Soc.* **2001**, *123*, 11318–11319. (b) Trindade, A. F.; Gois, P. M. P.; Veiros, L. F.; André, V.; Duarte, M. T.; Afonso, C. A. M.; Caddick, S.; Cloke, F. G. N. *J. Org. Chem.* **2008**, *73*, 4076–4086. (c) Kwak, J.; Kim, M.; Chang, S. *J. Am. Chem. Soc.* **2011**, *133*, 3780–3783. (d) Na, S. J.; Lee, B. Y.; Bui, N.-N.; Mho, S.; Jang, H.-Y. *J. Organomet. Chem.* **2007**, *692*, 5523–5527.

- (19) See also (a) Gois, P. M. P.; Trindade, A. F.; Veiros, L. F.; André, V.; Duarte, M. T.; Afonso, C. A. M.; Caddick, S.; Cloke, F. G. N. *Angew. Chem., Int. Ed.* **2007**, *46*, 5750–5753. (b) Trindade, A. F.; André, V.; Duarte, M. T.; Veiros, L. F.; Gois, P. M. P.; Afonso, C. A. M. *Tetrahedron* **2010**, *66*, 8494–8502.
- (20) Nakamura, E.; Yoshikai, N.; Yamanaka, M. *J. Am. Chem. Soc.* **2002**, *124*, 7181–7192.
- (21) Berry, J. F. *Dalton Trans.* **2012**, *41*, 700–713.
- (22) Kornecki, K. P.; Briones, J. F.; Boyarskikh, Y.; Fullilove, F.; Autschbach, J.; Schrote, K. E.; Lancaster, K. M.; Davies, H. M. L.; Berry, J. F. *Science* **2013**, *342*, 351–354.
- (23) Espino, C. G.; Fiori, K. W.; Kim, M.; Du Bois, J. *J. Am. Chem. Soc.* **2004**, *126*, 15378–15379.
- (24) Hashimoto, S.-I.; Watanabe, N.; Ikegami, S. *Tetrahedron Lett.* **1992**, *33*, 2709–2712.
- (25) (a) For a pertinent discussion and comparison with other rhodium catalysts, see Roizen, J. L.; Harvey, M. E.; Du Bois, J. *Acc. Chem. Res.* **2012**, *45*, 911–922. (b) See also Warzecha, E.; Berto, T. C.; Berry, J. F. *Inorg. Chem.* **2015**, *54*, 8817–8824.
- (26) For a preliminary communication, see Werlé, C.; Goddard, R.; Fürstner, A. *Angew. Chem., Int. Ed.* **2015**, *54*, 15452–15456.
- (27) For pioneering studies on the formation of (fairly stable) manganese carbenes by decomposition of aryl diazo derivatives, see (a) Herrmann, W. A. *Chem. Ber.* **1975**, *108*, 486–499. (b) Herrmann, W. A. *Angew. Chem., Int. Ed. Engl.* **1978**, *17*, 800–812.
- (28) Seidel, G.; Fürstner, A. *Angew. Chem., Int. Ed.* **2014**, *53*, 4807–4811.
- (29) (a) Seidel, G.; Gabor, B.; Goddard, R.; Heggen, B.; Thiel, W.; Fürstner, A. *Angew. Chem., Int. Ed.* **2014**, *53*, 879–882. (b) Seidel, G.; Mynott, R.; Fürstner, A. *Angew. Chem., Int. Ed.* **2009**, *48*, 2510–2513. (c) Fürstner, A. *Acc. Chem. Res.* **2014**, *47*, 925–938.
- (30) Staudinger, H.; Kupfer, O. *Ber. Dtsch. Chem. Ges.* **1911**, *44*, 2197–2212.
- (31) For the X-ray structure of **3a**, see Davis, P. J.; Harris, L.; Karim, A.; Thompson, A. L.; Gilpin, M.; Moloney, M. G.; Pound, M. J.; Thompson, C. *Tetrahedron Lett.* **2011**, *52*, 1553–1556.
- (32) Isolated **4a** was shown to undergo the same reaction at  $-10\text{ }^{\circ}\text{C}$ .
- (33) For a leading reference on the use of donor/donor rhodium carbenes in asymmetric synthesis, see Soldi, C.; Lamb, K. N.; Squitieri, R. A.; González-López, M.; Di Maso, M. J.; Shaw, J. T. *J. Am. Chem. Soc.* **2014**, *136*, 15142–15145.
- (34) Schwotzer, W.; von Philipsborn, W. *Helv. Chim. Acta* **1977**, *60*, 1501–1509.
- (35) In this context, it is noteworthy that the first free carbene to be characterized by X-ray diffraction also belonged to the donor/acceptor type; see Buron, C.; Gornitzka, H.; Romanenko, V.; Bertrand, G. *Science* **2000**, *288*, 834–836.
- (36) For recent advances, see (a) Qin, C.; Boyarskikh, V.; Hansen, J. H.; Hardcastle, K. I.; Musaev, D. G.; Davies, H. M. L. *J. Am. Chem. Soc.* **2011**, *133*, 19198–19204. (b) Negretti, S.; Cohen, C. M.; Chang, J. J.; Guptill, D. M.; Davies, H. M. L. *Tetrahedron* **2015**, *71*, 7415–7420.
- (37) Unfortunately, however, this product is prone to rapid epimerization during flash chromatography.
- (38) Related electrophilic gold and platinum carbenes exhibit considerable nonclassical carbocation character; see (a) Fürstner, A.; Szilatt, H.; Gabor, B.; Mynott, R. *J. Am. Chem. Soc.* **1998**, *120*, 8305–8314. (b) Fürstner, A.; Stelzer, F.; Szilatt, H. *J. Am. Chem. Soc.* **2001**, *123*, 11863–11869. (c) Fürstner, A.; Davies, P. W.; Gress, T. *J. Am. Chem. Soc.* **2005**, *127*, 8244–8245. (d) Fürstner, A.; Aissa, C. *J. Am. Chem. Soc.* **2006**, *128*, 6306–6307. (e) Fürstner, A.; Morency, L. *Angew. Chem., Int. Ed.* **2008**, *47*, 5030–5033.
- (39) (a) Fürstner, A.; Davies, P. W. *Angew. Chem., Int. Ed.* **2007**, *46*, 3410–3449. (b) Fürstner, A. *Chem. Soc. Rev.* **2009**, *38*, 3208–3221.
- (40) For reviews on diazoalkane metal complexes, see (a) Sutton, D. *Chem. Rev.* **1993**, *93*, 995–1022. (b) Mizobe, Y.; Ishii, Y.; Hidai, M. *Coord. Chem. Rev.* **1995**, *139*, 281–311. (c) Dartiguenave, M.; Menu, M. J.; Deydier, E.; Dartiguenave, Y.; Siebald, H. *Coord. Chem. Rev.* **1998**, *178–180*, 623–663.
- (41) (a) Complex **14** shows a rather short C1–N1 bond (1.274(11) Å) and a fairly long N1–N2 bond (1.362(10) Å); these data suggest that this adduct is close to the “hydrazinato” resonance extreme of diazoalkane complexes; for pertinent discussions see ref **40** and the following: Hidai, M.; Mizobe, Y.; Sato, M.; Kodama, T.; Uchida, Y. *J. Am. Chem. Soc.*, **1978**, *100*, 5740–5748. We find no evidence of residual electron density in the vicinity of N1 which might indicate the presence of H-atoms. (b) It is noteworthy that the conformation of the esp ligands is different from that in **10** but similar to that of the known adduct  $[\text{Rh}_2(\text{esp})_2](\text{acetone})_2$  (cf. ref **23**).
- (42) For an interesting example in which a diazo compound gets ligated end-on to copper but the resulting complex eventually transforms into a true copper donor/acceptor carbene upon raising the temperature, see Pereira, A.; Champouret, Y.; Martin, C.; Álvarez, E.; Etienne, M.; Belderrain, T. R.; Pérez, P. *J. Chem. - Eur. J.* **2015**, *21*, 9769–9775.
- (43) For representative catalytic reactions involving Rh(I) carbenes, see the following and literature cited therein: (a) Werner, H.; Schneider, M. E.; Bosch, M.; Wolf, J.; Teuben, J. H.; Meetsma, A.; Troyanov, S. *Chem. - Eur. J.* **2000**, *6*, 3052–3059. (b) Tsoi, Y.-T.; Zhou, Z.; Yu, W.-Y. *Org. Lett.* **2011**, *13*, 5370–5373. (c) Demonceau, A.; Simal, F.; Noels, A. F.; Vinas, C.; Nunez, R.; Teixidor, F. *Tetrahedron Lett.* **1997**, *38*, 7879–7882. (d) Chen, D.; Zhang, X.; Qi, W.-Y.; Xu, B.; Xu, M.-H. *J. Am. Chem. Soc.* **2015**, *137*, 5268–5271. (e) Xia, Y.; Liu, Z.; Feng, S.; Ye, F.; Zhang, Y.; Wang, J. *Org. Lett.* **2015**, *17*, 956–959. (f) Yada, A.; Fujita, S.; Murakami, M. *J. Am. Chem. Soc.* **2014**, *136*, 7217–7220. (g) Nishimura, T.; Maeda, Y.; Hayashi, T. *Angew. Chem., Int. Ed.* **2010**, *49*, 7324–7327. (h) Chen, D.; Zhu, D.-X.; Xu, M.-H. *J. Am. Chem. Soc.* **2016**, *138*, 1498–1501.
- (44) For representative catalytic reactions involving Rh(III) carbenes, see the following and literature cited therein: (a) Callot, H. J.; Piechocki. *Tetrahedron Lett.* **1980**, *21*, 3489–3492. (b) Callot, H. J.; Metz, F.; Piechocki, C. *Tetrahedron* **1982**, *38*, 2365–2369. (c) O'Malley, S.; Kodadek, T. *Tetrahedron Lett.* **1991**, *32*, 2445–2448. (d) Hayashi, T.; Kato, T.; Kaneko, T.; Asai, T.; Ogoshi, H. *J. Organomet. Chem.* **1994**, *473*, 323–327. (e) Lo, V. K.-Y.; Thu, H.-Y.; Chan, Y.-M.; Lam, T.-L.; Yu, W.-Y.; Che, C.-M. *Synlett* **2012**, *23*, 2753–2757. (f) Franssen, N. M. G.; Finger, M.; Reek, J. N. H.; de Bruin, B. *Dalton Trans.* **2013**, *42*, 4139–4152.
- (45) Chan, W.-W.; Lo, S.-F.; Zhou, Z.; Yu, W.-Y. *J. Am. Chem. Soc.* **2012**, *134*, 13565–13568.
- (46) See the following for leading references and literature cited therein: (a) Shi, Z.; Koester, D. C.; Bouldadakis-Arapinis, M.; Glorius, F. *J. Am. Chem. Soc.* **2013**, *135*, 12204–12207. (b) Liang, Y.; Yu, K.; Li, B.; Xu, S.; Song, H.; Wang, B. *Chem. Commun.* **2014**, *50*, 6130–6133. (c) Jeong, J.; Patel, P.; Hwang, H.; Chang, S. *Org. Lett.* **2014**, *16*, 4598–4601. (d) Hu, F.; Xia, Y.; Ye, F.; Liu, Z.; Ma, C.; Zhang, Y.; Wang, J. *Angew. Chem., Int. Ed.* **2014**, *53*, 1364–1367. (e) Ye, B.; Cramer, N. *Angew. Chem., Int. Ed.* **2014**, *53*, 7896–7899. (f) Shi, J.; Yan, Y.; Li, Q.; Xu, H. E.; Yi, W. *Chem. Commun.* **2014**, *50*, 6483–6486. (g) Yang, Y.; Wang, X.; Li, Y.; Zhou, B. *Angew. Chem., Int. Ed.* **2015**, *54*, 15400–15404. (h) Zhou, J.; Shi, J.; Liu, X.; Jia, J.; Song, H.; Xu, H. E.; Yi, W. *Chem. Commun.* **2015**, *51*, 5868–5871. (i) Iagafarova, I. E.; Vorobyeva, D. V.; Peregodov, A. S.; Osipov, S. N. *Eur. J. Org. Chem.* **2015**, *2015*, 4950–4955. (j) Wang, L.; Li, Z.; Qu, X.; Peng, W.-M.; Hu, S.-Q.; Wang, H.-B. *Tetrahedron Lett.* **2015**, *56*, 6214–6218. (k) Ai, W.; Yang, X.; Wu, Y.; Wang, X.; Li, Y.; Yang, Y.; Zhou, B. *Chem. - Eur. J.* **2014**, *20*, 17653–17657. (l) Sharma, S.; Han, S. H.; Han, S.; Ji, W.; Oh, J.; Lee, S.-Y.; Oh, J. S.; Jung, Y. H.; Kim, I. S. *Org. Lett.* **2015**, *17*, 2852–2855. (m) Zhang, Y.; Zheng, J.; Cui, S. *J. Org. Chem.* **2014**, *79*, 6490–6500. (n) Yu, S.; Liu, S.; Lan, Y.; Wan, B.; Li, X. *J. Am. Chem. Soc.* **2015**, *137*, 1623–1631. (o) Cheng, Y.; Bolm, C. *Angew. Chem., Int. Ed.* **2015**, *54*, 12349–12352. (p) Zhou, B.; Chen, Z.; Yang, Y.; Ai, W.; Tang, H.; Wu, Y.; Zhu, W.; Li, Y. *Angew. Chem., Int. Ed.* **2015**, *54*, 12121–12126.
- (47) For a pertinent silver-free case, see Hyster, T. K.; Ruhl, K. E.; Rovis, T. *J. Am. Chem. Soc.* **2013**, *135*, 5364–5367.
- (48) See the following for leading references and the literature cited therein: (a) Padwa, A.; Kassir, J. M.; Xu, S. L. *J. Org. Chem.* **1991**, *56*,



- 6971–6972. (b) Chen, J.; Ma, S. *Chem. - Asian J.* **2010**, *5*, 2415–2421.
- (c) Cui, X.; Xu, X.; Wojtas, L.; Kim, M. M.; Zhang, X. P. *J. Am. Chem. Soc.* **2012**, *134*, 19981–19984. (d) Breslow, R.; Winter, R.; Battiste, M. *J. Org. Chem.* **1959**, *24*, 415–416.
- (49) (a) Davies, H. M. L.; Romines, K. R. *Tetrahedron* **1988**, *44*, 3343–3348. (b) Müller, P.; Gränicher, C. *Helv. Chim. Acta* **1993**, *76*, 521–534.
- (50) Ma, S.; Lu, L.; Lu, P. *J. Org. Chem.* **2005**, *70*, 1063–1065.
- (51) For a C-metalated Rh(III) enolate prepared by an entirely different route, see Wu, J.; Bergman, R. G. *J. Am. Chem. Soc.* **1989**, *111*, 7628–7630.
- (52) Braun, M. *Modern Enolate Chemistry. From Preparation to Applications in Asymmetric Synthesis*; Wiley-VCH: Weinheim, 2016.
- (53) Maxwell, J.; Kodadek, T. *Organometallics* **1991**, *10*, 4–6.
- (54) For a related chloride migration to the carbene center in the platinum series, see Bergamini, P.; Costa, E.; Sostero, S.; Orpen, A. G.; Pringle, P. G. *Organometallics* **1991**, *10*, 2989–2990.